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2018 DOE Vehicle Technologies Office Annual Merit Review

SEI Stabilization (SEISta): Synthesis and Stability of Lithium Silicate and Its Interaction with the Solid-Electrolyte Interface (SEI)

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Sandia National Laboratories

June 20th, 2018

Project ID BAT348



Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Timeline

- October 1st 2016 - September 30st 2019.
- Percent complete: 40%

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
 - Cost, Performance and Safety

Partners

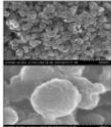
- The SEISta Team
 - National Renewable Energy Laboratory
 - Sandia National Laboratory
 - Argonne National Laboratory
 - Oak Ridge National Laboratory
 - Lawrence Berkeley National Laboratory
- UC Berkeley
- Colorado University Boulder
- Colorado School of Mines

Budget

- Funding for FY 18: \$3900K

From USDrive 2017 Roadmap

Advanced Battery Materials Research
TRL 2-3



Participants

- National Laboratories
- Universities & Industry
- Battery500 Consortium

Battery Materials Research Areas

- High capacity/high voltage cathodes
- Alloys & lithium metal anodes
- Material diagnostics and modelling

Battery Materials Targets

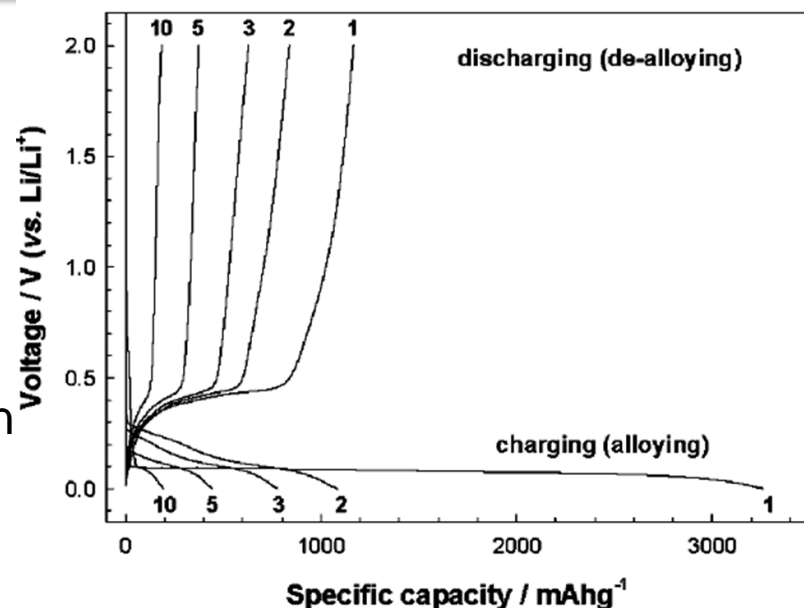
- Cathode capacity >300mAh/g
- Anode capacity >1,000mAh/g
- High-voltage cathodes & 5V stable electrolytes
- Solid-polymer electrolytes with >10⁻³ S/cm ionic conductivity

Program Relevance

- Si anodes are ~10x higher capacity than graphite anodes
- Si anodes have two challenges
 - High Capacity Fade
 - Poor Shelf Life
- SEI formation in Si much more complex than in graphite, and seems to be dependent on initial state and history
 - Large volume expansion on alloying
- Silicates are (sometimes) seen to play a role
 - Data is inconclusive
- Alloy formation should require some lithiation of the oxide to occur
 - Kristen Persson, LBNL (BAT344) talk for more on this

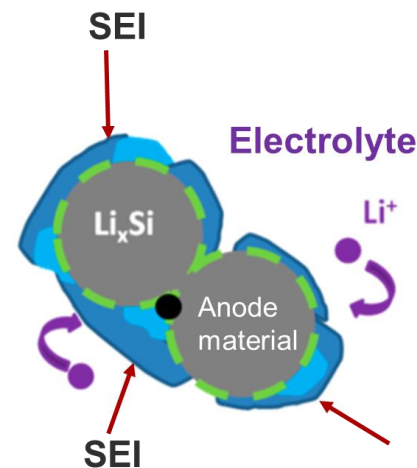
Objective:

Using Li-Silicate Model systems to help understand the formation and evolution of Si SEI both chemically and electrochemically

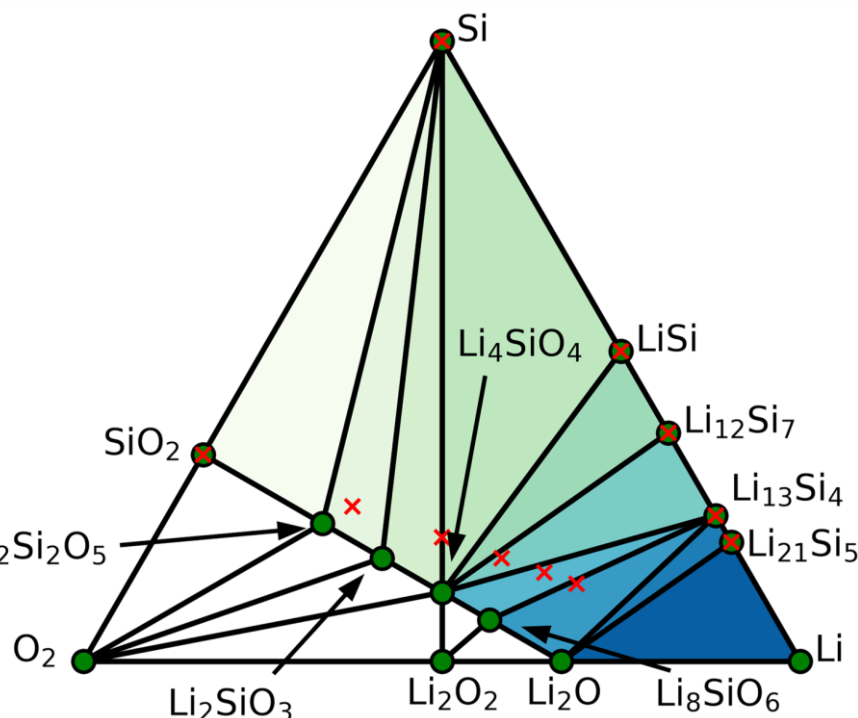


Si composite half-cell cycled at 100 mA/g current density at room temp

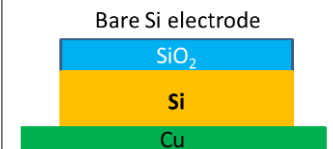
Ryu, J. H., J. W. Kim, Y. E. Sung and S. M. Oh (2004). [Electrochemical and Solid State Letters](#)



Li-Silicate Relevance



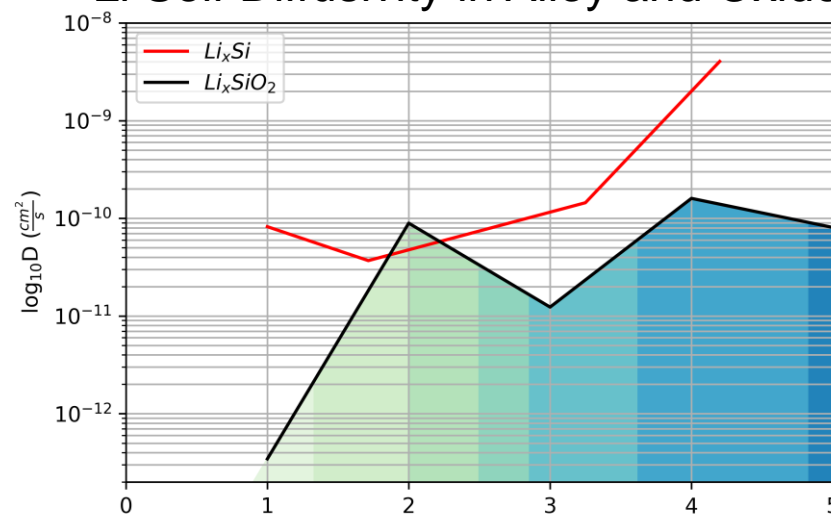
Kim, S.Y. and Y. Qi, *Property Evolution of Al₂O₃ Coated and Uncoated Si Electrodes: A First Principles Investigation*. Journal of the Electrochemical Society, 2014. **161**(11): p. F3137-F3143.



Lithiation Reaction	$2\text{Li} + \text{SiO}_2 \rightarrow 0.5\text{Li}_4\text{SiO}_4 + 0.5\text{Si}$ $\langle V \rangle = 1.13\text{V}$	
Young's Modulus variation due to lithiation	$E(\alpha\text{-SiO}_2) = 118.3\text{ GPa}$ $E(\text{Li}_4\text{SiO}_4) = 141.1\text{ GPa}$	
Energy barrier of Li migration	SiO ₂	15.53 kJ/mol
	Li ₂ Si ₂ O ₅	56.15 kJ/mol
	Li ₂ SiO ₃	27.70 kJ/mol
	Li ₄ SiO ₄	21.17 kJ/mol

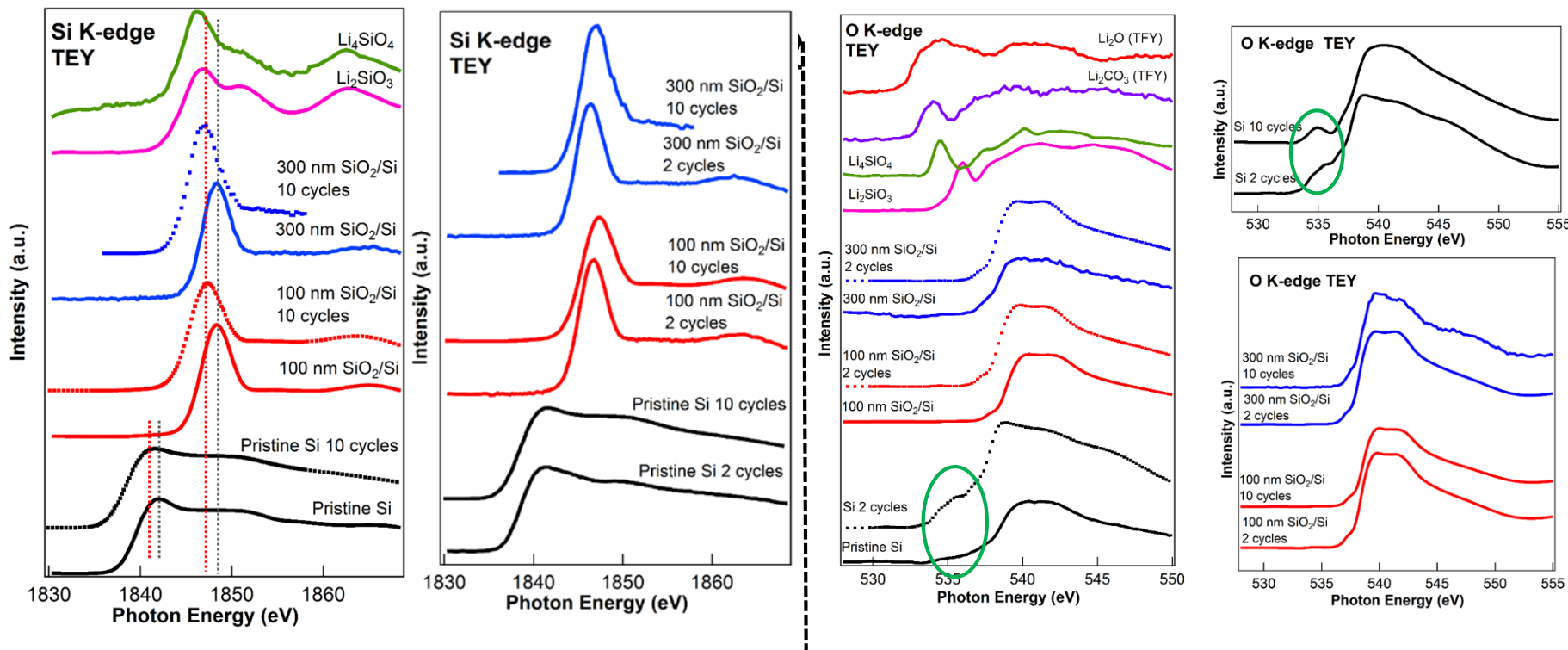
- SiO₂ should go through a number of silicates, each with their own transport
- What silicate forms should influence subsequent growth

Li Self Diffusivity in Alloy and Oxide



From LBNL, Persson, BAT344

Do Silicates Even Appear?



- Si K-edge, the features shift to lower energy due to the lithiation process.
 - The spectra shapes after lithiation are different from that of Li_4SiO_4 and Li_2SiO_3 (*Reference spectra are from commercially available powders*).
- O K-edge, Li_2O formation after 2 and 10 cycles was observed for pristine Si.
 - For oxide samples, no features of Li_2SiO_3 and Li_4SiO_4 are observed, consistent with Si K-edge results.
 - No Li_2O is formed for all the cycled oxide samples.
- No indication of formation of lithium silicates

From LBNL, Kostecki, et. al., BAT346

Milestones

Quarter 1 Milestone:

Have completed the selection and characterization (XPS, SIMS, IR, and Raman), including determination of the surface termination chemistry and impurity levels, of the SEISta model research samples to be used by all members of the team in FY18. **100% complete**

Quarter 2 Milestone:

Have characterized (XPS, SIMS, IR, and Raman) the surface chemistry and composition of the SEISta model research samples after contact with the electrolyte, before cycling, including the nature of the electrolyte decomposition products. **100% complete**

Quarter 3 Milestone:

Completed characterization (electrochemistry, IR and Raman) of the early stage silicon electrolyte interphase formation on the SEISta model research samples, specifically by establishing and demonstrating a procedure for quantitatively measuring the solubility of SEI on silicon surfaces.

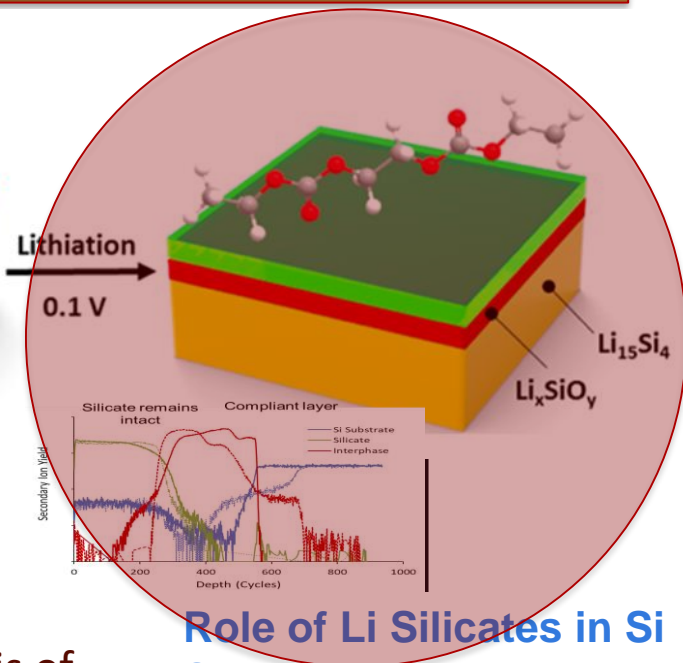
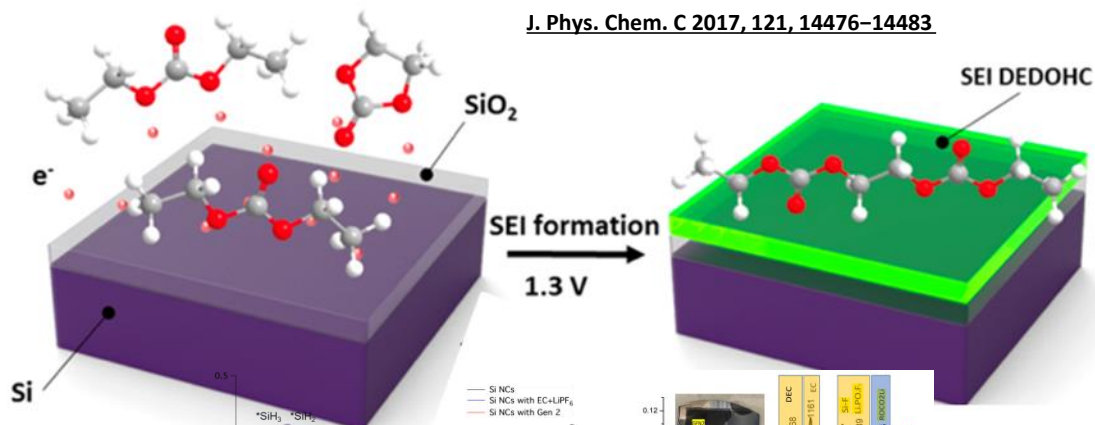
Quarter 4 Milestones:

Established and demonstrated a procedure for measuring the growth rate of silicon SEI components at fixed potentials and during cycling.

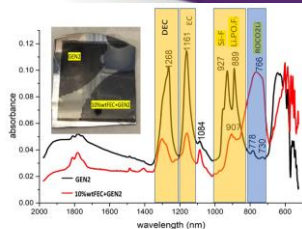
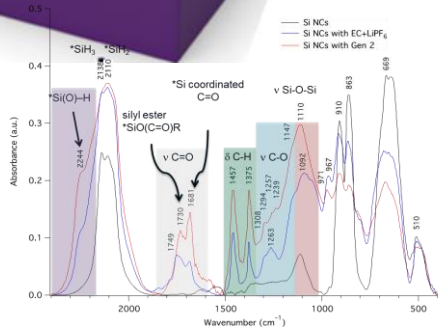
Have determined how the physical properties of the silicon electrolyte interface are influenced by the nature of the silicon surface on the SEISta model samples.

Chemical reactivity vs electrochemical reactivity

J. Phys. Chem. C 2017, 121, 14476–14483



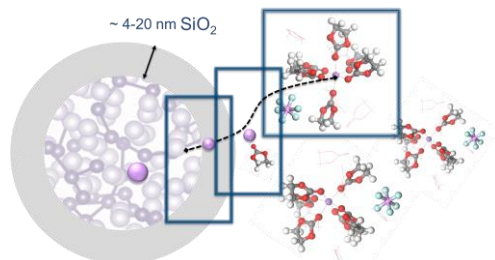
Chemical Reactivity of Silicon
Project ID BAT345



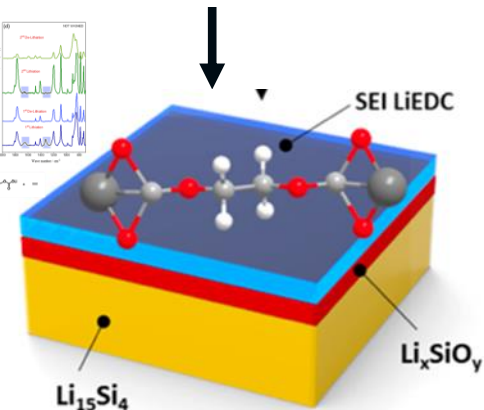
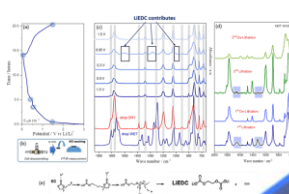
Surface analysis of the Silicon SEI
ID BAT347

Role of Li Silicates in Si SEI Formation ID BAT348

Spectroelectrochemistry on silicon ID BAT364



Predicting and Understanding Novel Electrode Materials From First-Principles Project ID BAT344



Milestones Mapping to Silicates

FY18Q1

Samples

FY18Q2

Exposure

FY18Q3

Stability

FY18Q4

Performance

Program Milestones

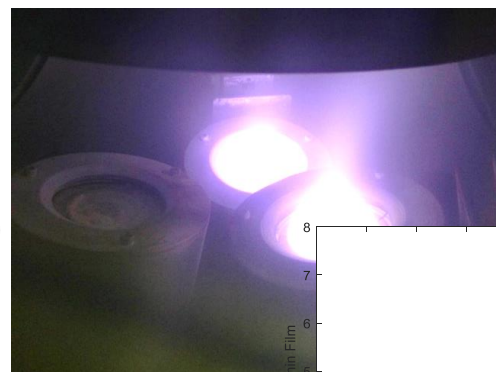
Determine starting surface state of model research samples	Characterize surface after exposure to electrolytes	Characterize Early Stage Interphase by Measuring Solubility of SEI	Establish Growth rate of Si SEI components as $f(V, N)$
Characterize at Each Step with Surface Techniques: SIMS, XPS, ATRIR, RAMAN, ECAFM			

Li-Silicate Study Milestones

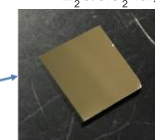
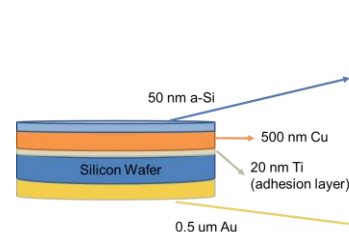
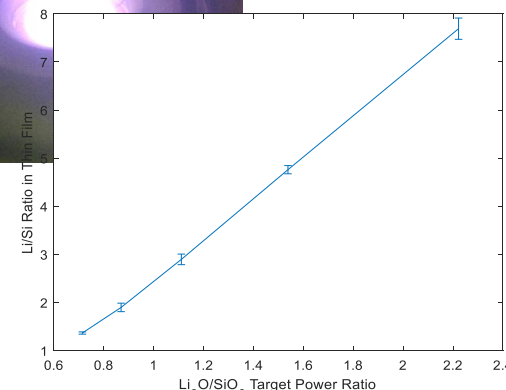
	FY18Q1	FY18Q2	FY18Q3	FY18Q4	FY19Q1	FY19Q2	FY19Q3	FY19Q4
Establish Base Sample and Model $\text{Li}_x\text{Si}_y\text{O}_z$ film growth								
Expose to Electrolyte for various times, characterize								
Expose to Electrolyte and measure impedance as $f(T)$								
Follow C/D protocols with temp based impedance at High and Low SOC								
Extend Characterization of Surfaces to Electrochemically Cycled Surfaces								
Complete ECAFM characterization of Chemically and Electrochemically Cycled surfaces								
Correlation of Kinetics to Surface Chemistry observed through ATRIR/SIMS/XPS								
Correlate Mechanics of ECAFM to Observed Chemistry								

Approach

- Standardize the Si substrate
 - 50nm silicate/50nm Si/500nm Cu/650um D-Si/500nm Au
 - Samples from Gabe Vieth, ORNL (BAT 345)
- Sputter to generate **controlled composition model films**
- Parallelize Analysis across compositions to look for differences
 - Use easy to assemble architectures for sample recovery
 - Standardize Test Cell for reproducibility
 - Design from Rob Kostecki, LBNL (BAT 346) and Chunmei Ban, NREL (BAT 347)
- Study evolved surfaces using SIMS/XPS/ATRIR/ECAFM
- Recover kinetics in chemical and electrochemical methods through rate limiting energies

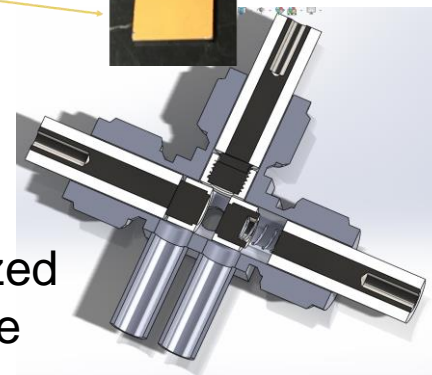


PVD for
composition
control

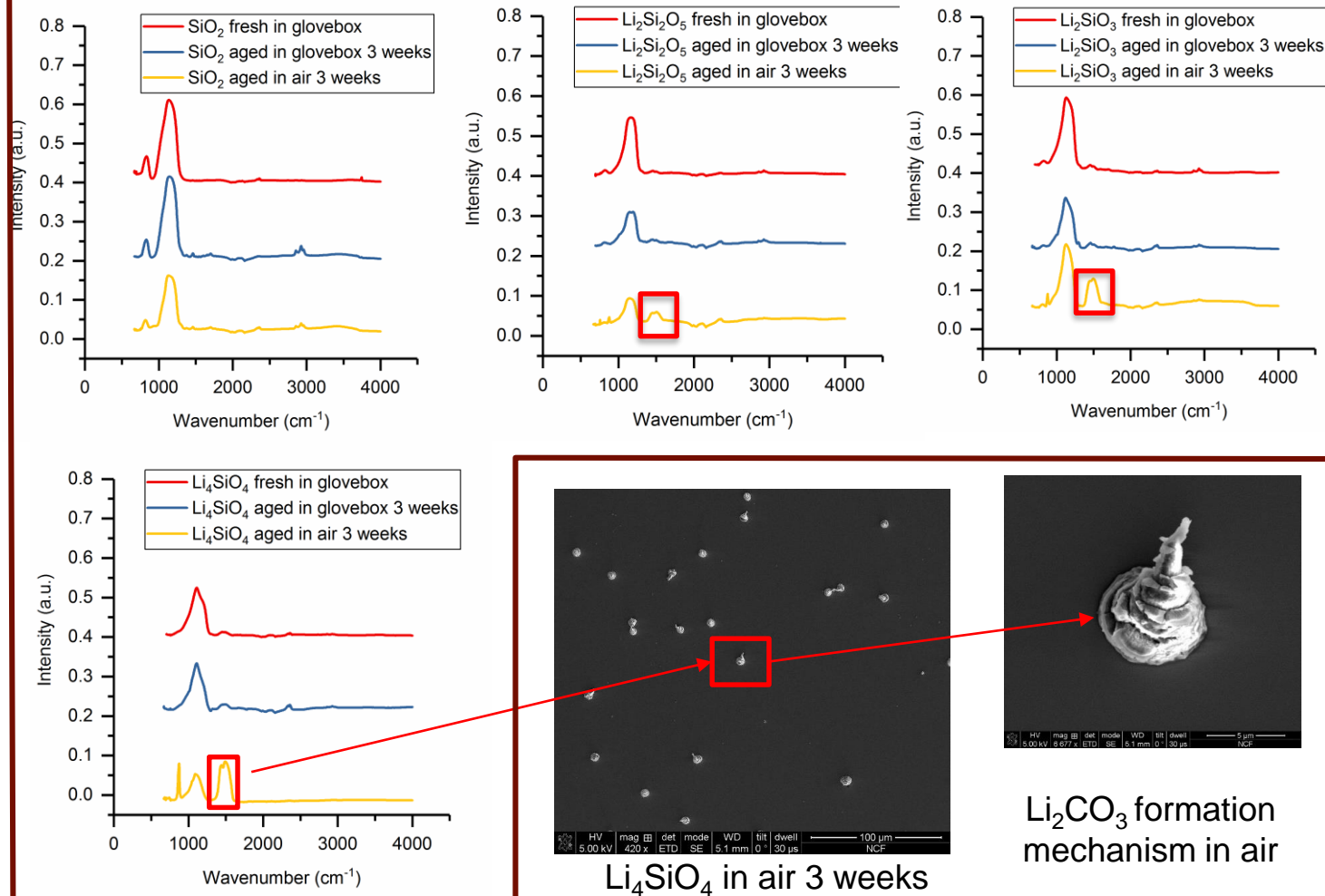


Standard
Samples

Well
characterized
architecture

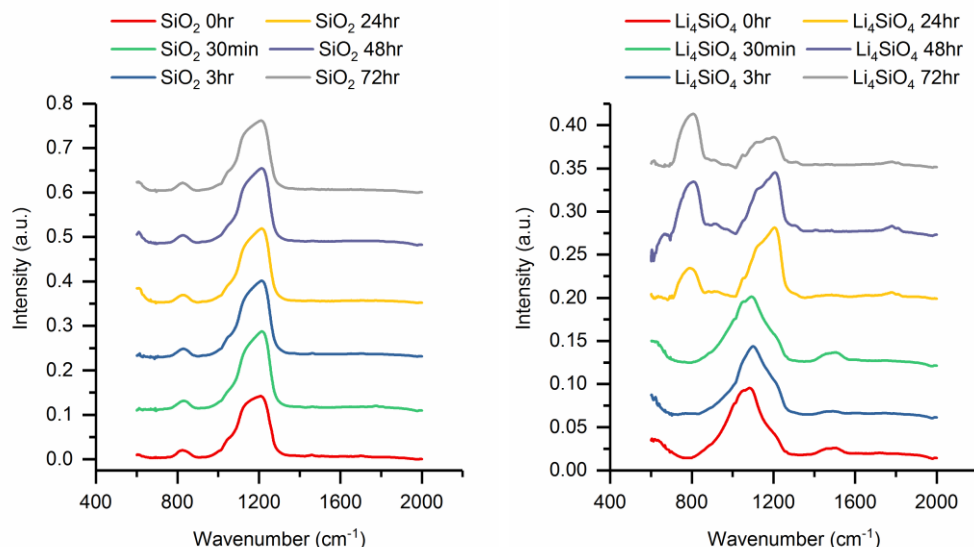


Sample Stability (Milestone 1)

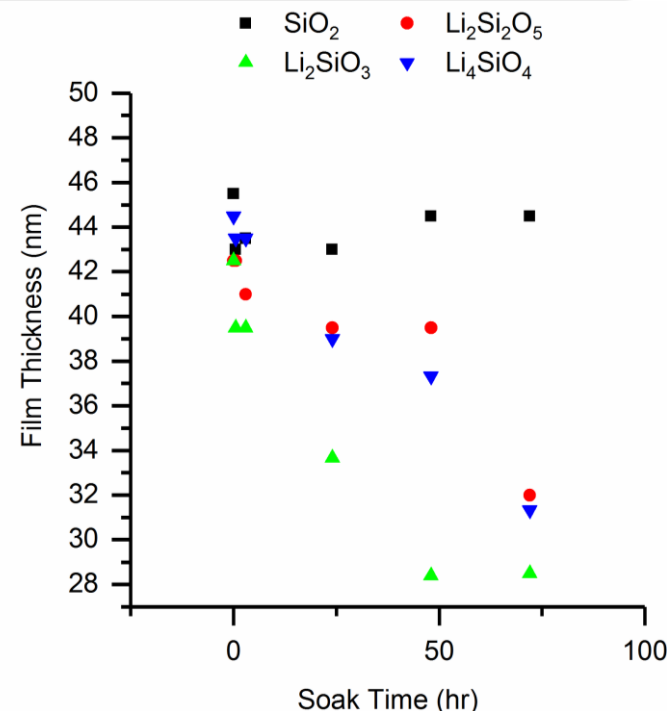


The more Li in the silicate, the more sensitivity to oxygen and moisture sensitivity
Working with samples in inert conditions provides stability
Air exposure should be minimized

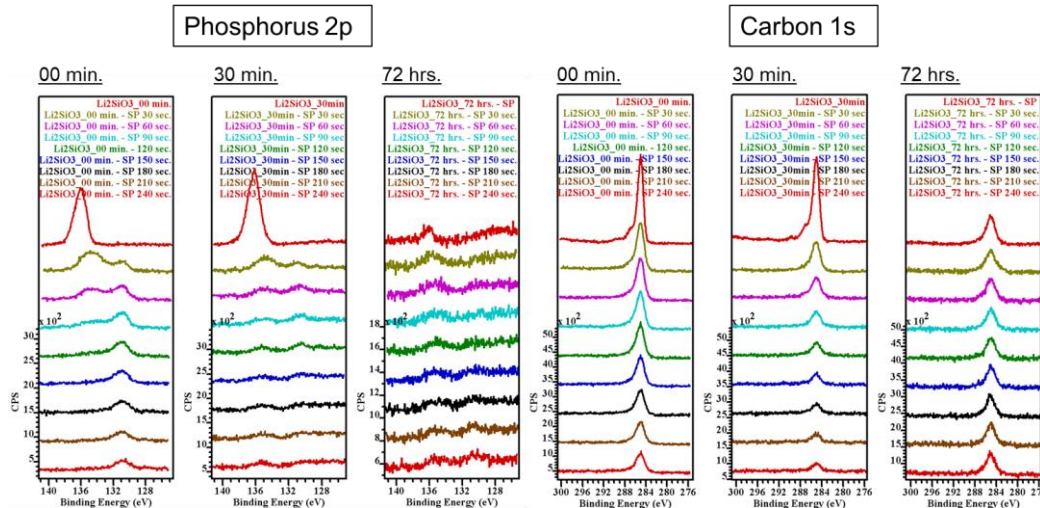
Electrolyte Exposure (Milestone 2)



ATRIR: lithium silicates appears to be more reactive than the SiO₂



FIB-SEM: Similar to ATRIR

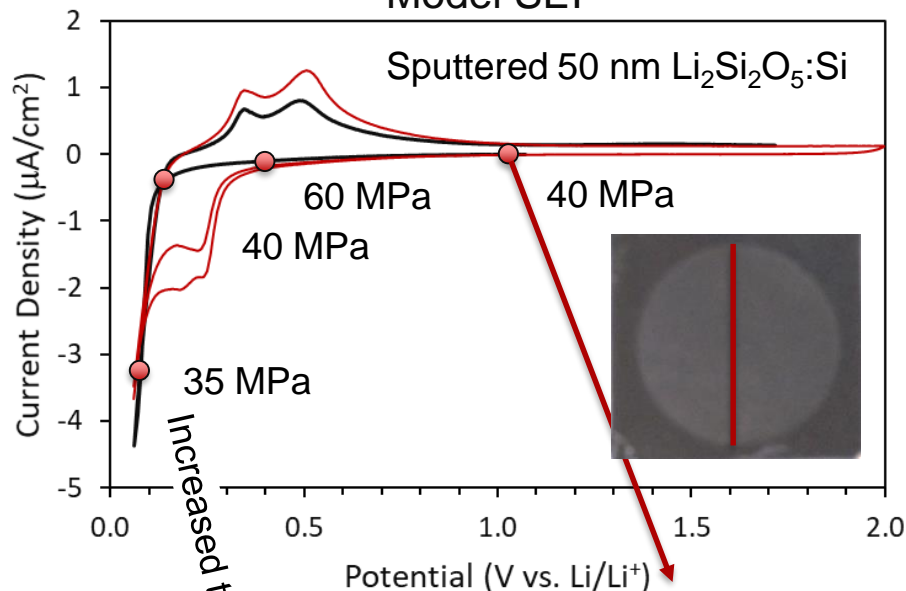


XPS: Some evidence of film evolution (P and C peaks seem to be much lower after longer electrolyte exposure)

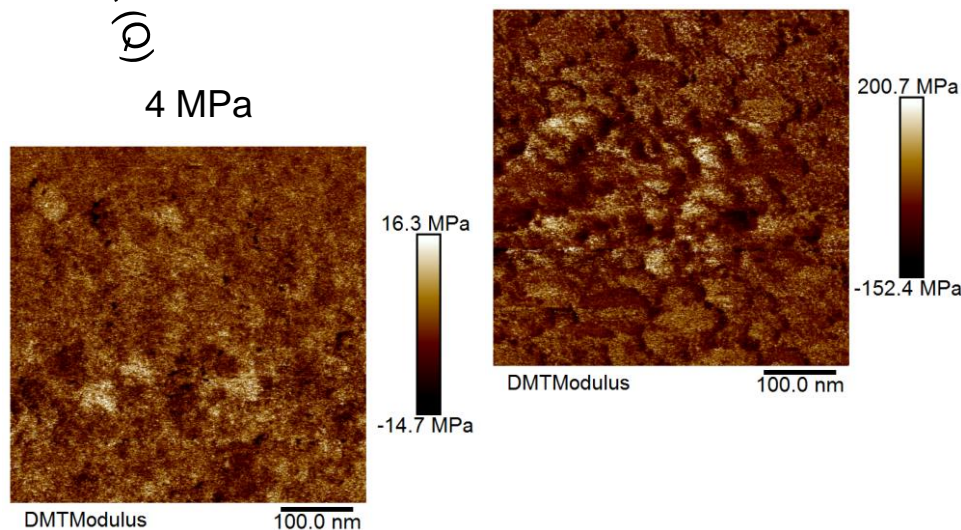
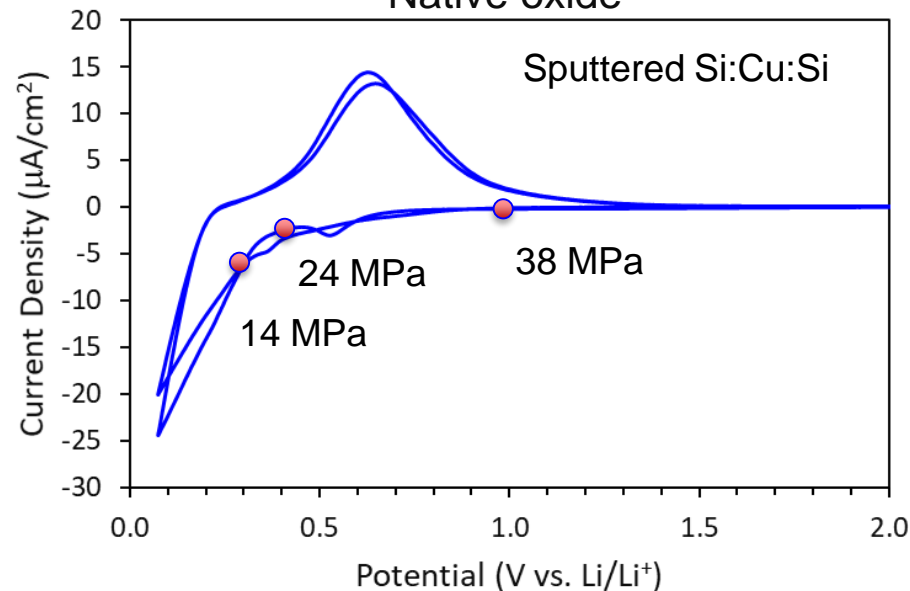
- Li-Silicate evolves differently than SiO₂
- Presence (or absence) of Li-Silicate could change SEI formation over time

Mechanical Response of Silicates

Model SEI



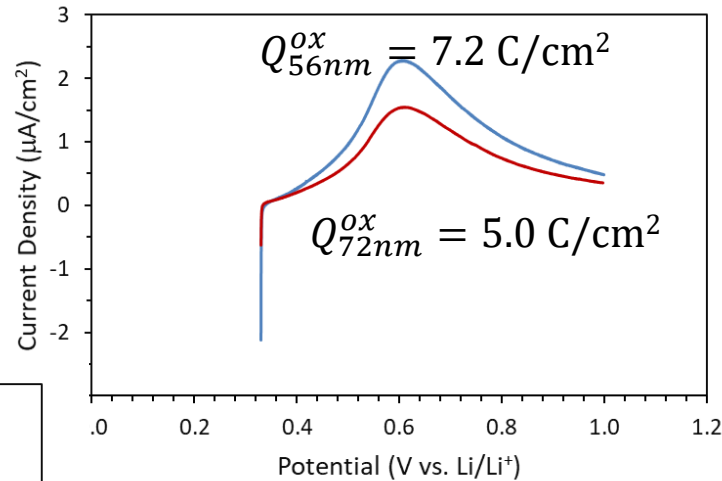
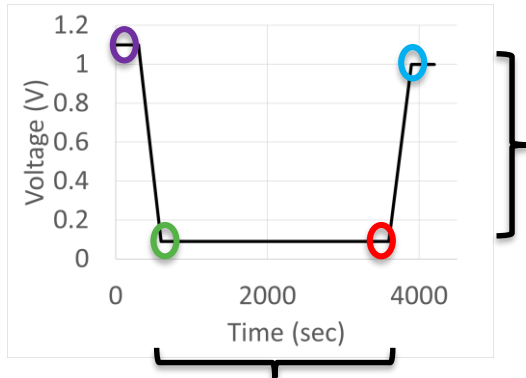
Native oxide



- Decreasing modulus of the surface is normal for alloying
- Silicates do not become compliant (initially)
- There is a temporal response that increases compliance of the silicate film over time

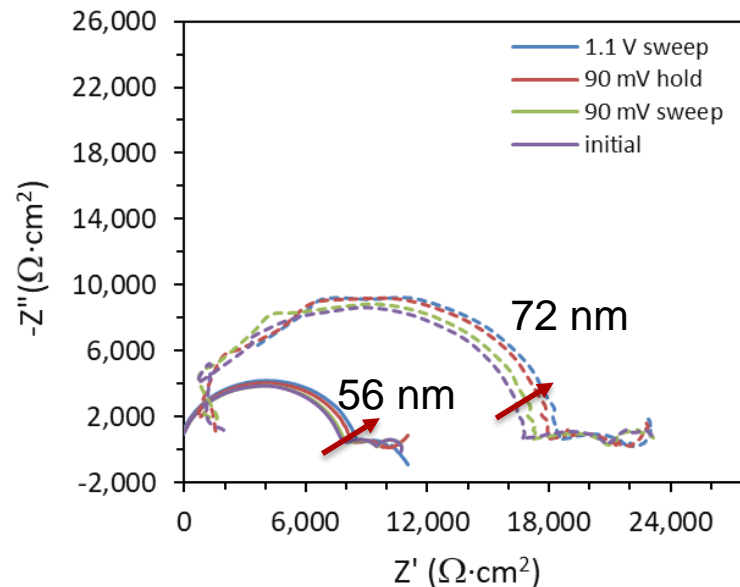
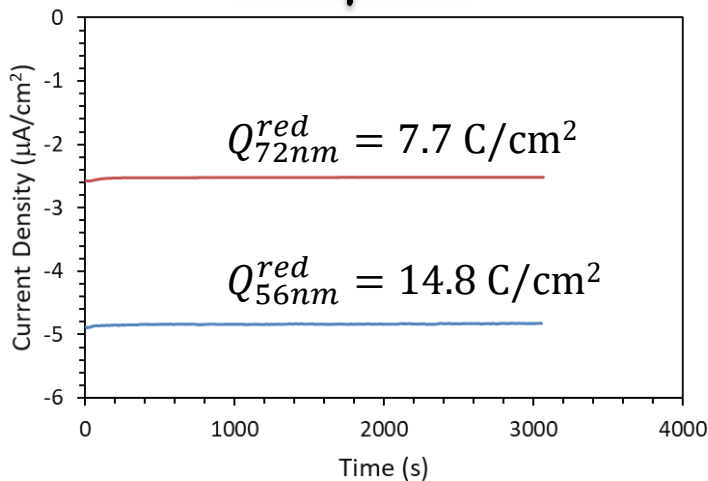
$\text{Li}_x\text{Si}_y\text{O}$ Coherence with Cycling

Initial OC = 1.1 V vs. $\text{Li}^{0/+}$



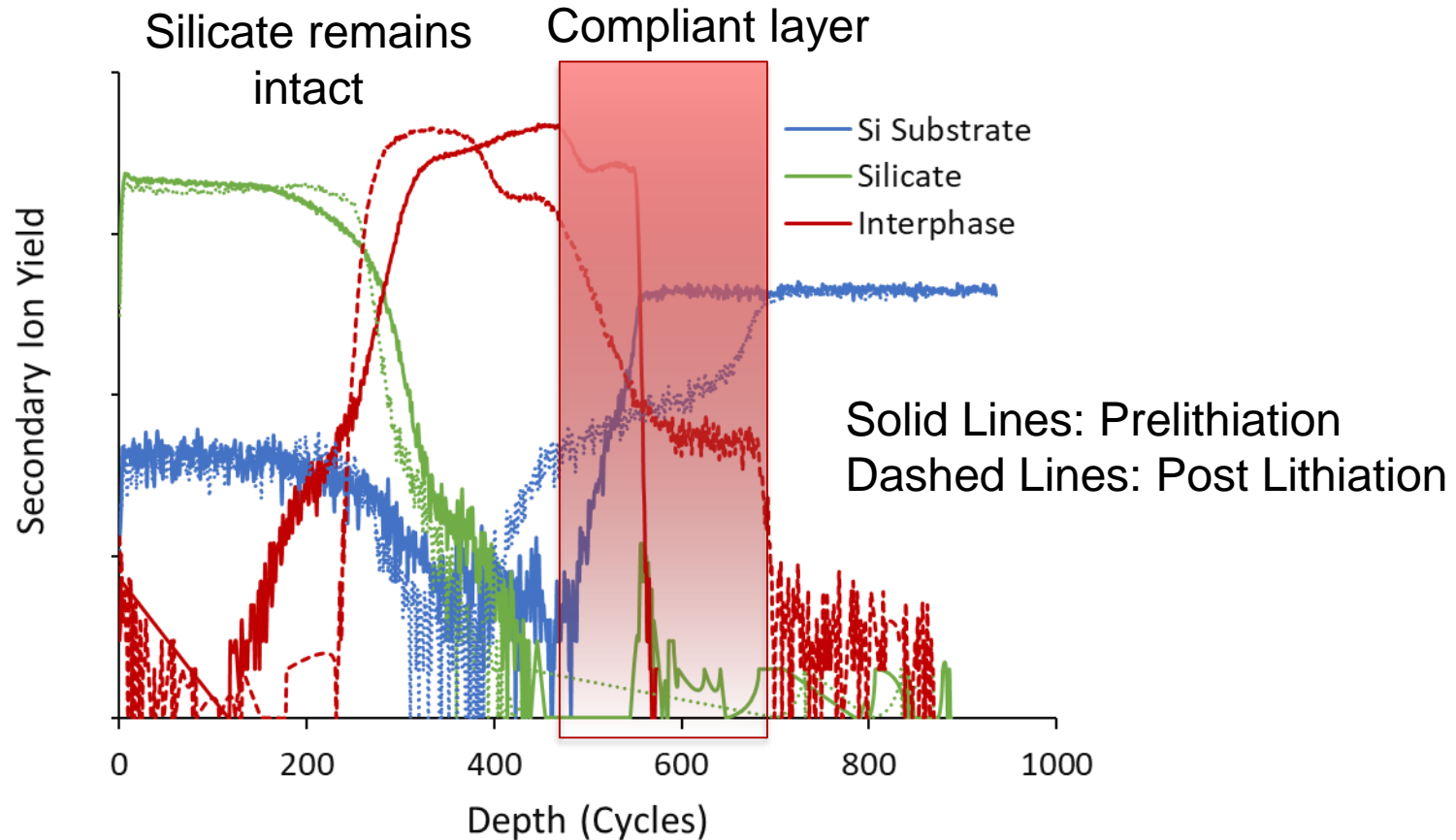
- Impedance scales with silicate thickness
- Current at constant field scales with thickness

∴ **Silicate film remains ionically coherent, regulating the current**



SIMS Profiles show Underlayer

$\text{Li}_2\text{Si}_2\text{O}_3$ Over 50nm Si

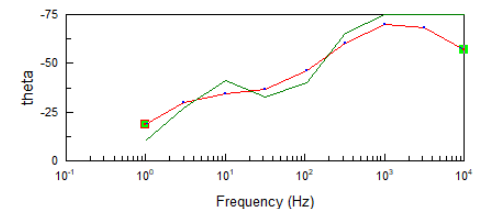
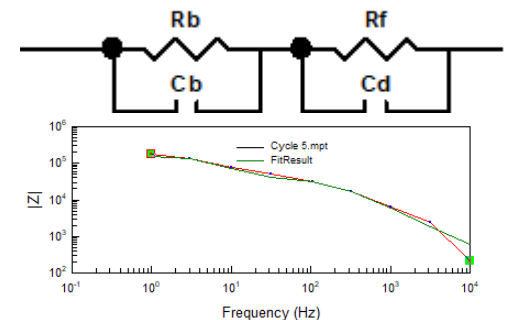
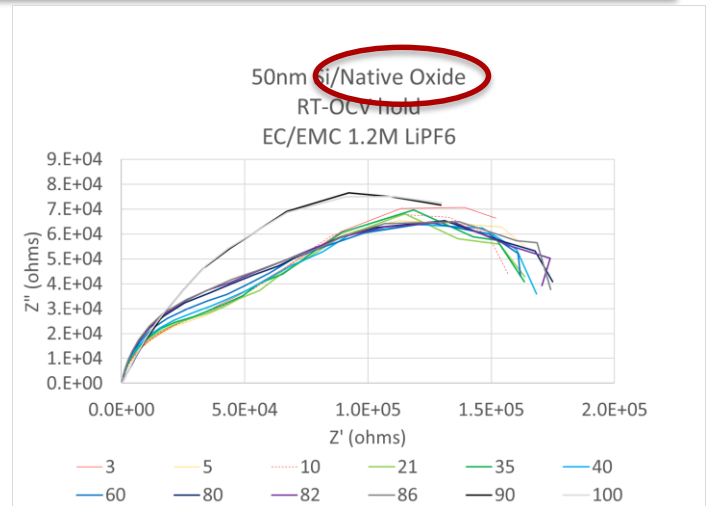


A layer, under the silicate, appears after lithiation that does not disrupt the silicate

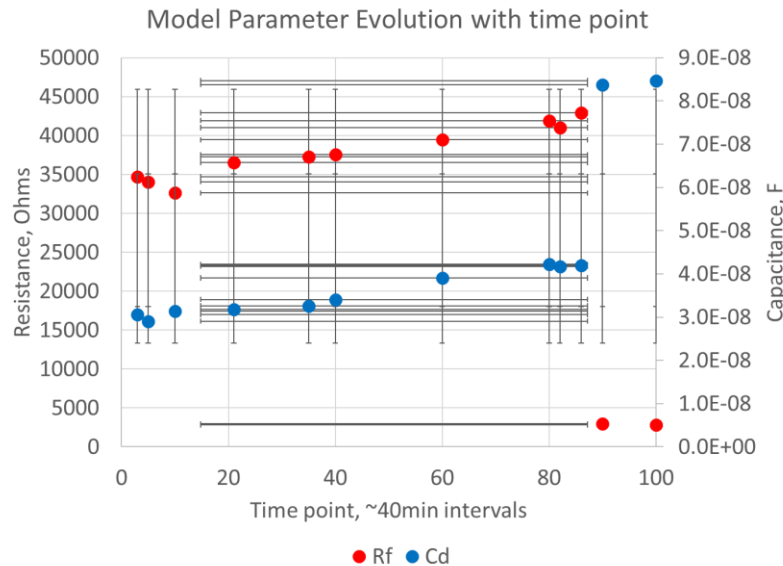
Time Evolution of SEI Formation

- EIS 10kHz-0.1Hz, 10mV PP
- Hold 30m between EIS observations
- Watch impedance change over time
- Appears as slow change in R_f and C_d , until several days in, then relatively sudden change to much higher C_d and much lower R_f
- Model with classic flat surface to bulk electrolyte model

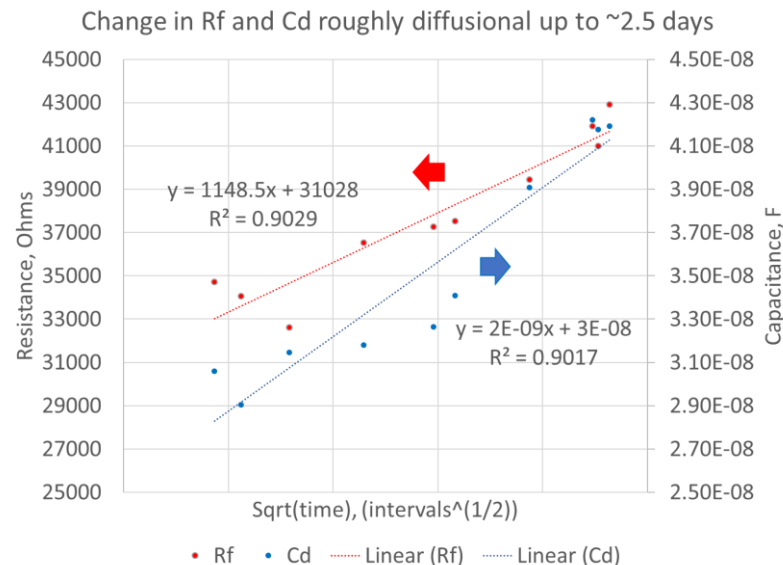
Impedance is changing over with just electrolyte exposure
This change is not simple diffusion limited kinetics



Change Appears Surface Related

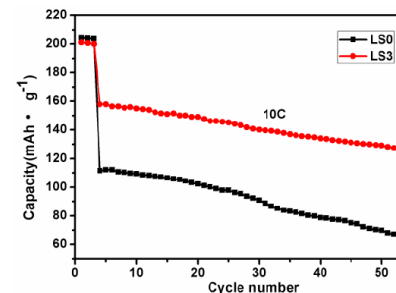
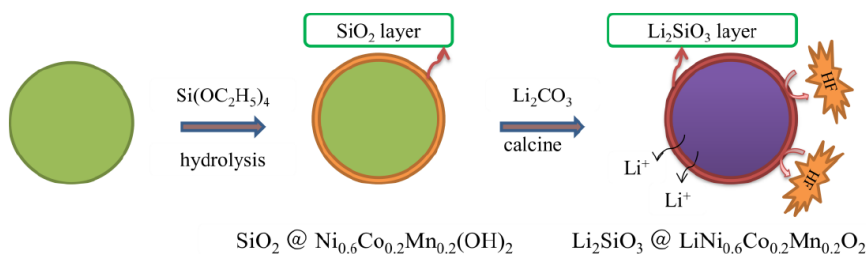


- A possible hypothesis:
- Starting with native oxide
- SEI grows normally to a given extent of time/thickness
- Formation of compliant underlayer appears after this time/thickness
- Underlayer “protects” outer SEI from further evolution
- Need further time evolution
- Impact of silicates?
- Impact of Lithiation and curved surfaces?

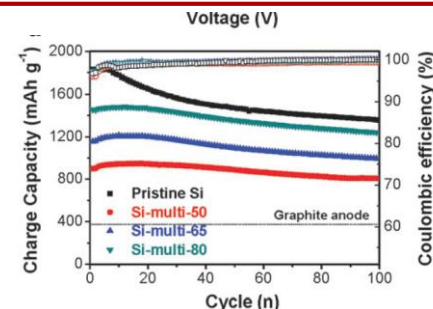
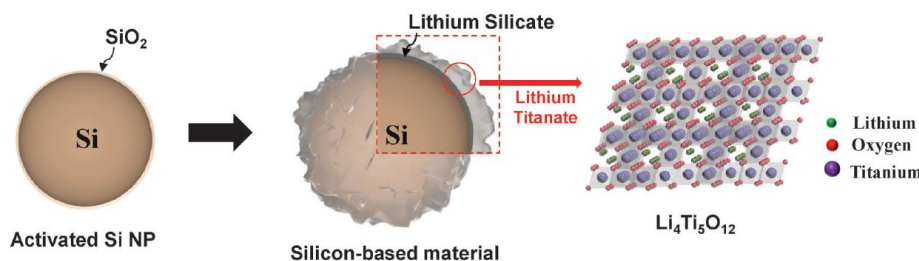


Underlayer formation *may* cause discontinuous change in impedance
Do silicates behave similarly?

Comparison to Powders



Wang *et al.* Electrochimica Acta 2016, 222, 806-813



Lee *et al.* Energy Environ. Sci. 2015, 8, 2075-2084

- Data from ANL, Zhang, BAT352
 - Silicate coatings seem to decrease first cycle loss, lithium ion conductivity, and stability against electrolyte
- Silicates, if they exist, are having an effect in the powders, too

Response to Previous FY Comments Sandia National Laboratories

- First Year Reviewed

CONTRIBUTORS AND ACKNOWLEDGMENT

Alison Dunlop	Dennis Dees	Jinghua Guo	Robert Kostecki
Al-Jassim, Mowafak	Eric Allcorn	John Moseley	Robert Tenent
Andrew Jansen	Fulya Dogan Key	Kaigi Nie	Sang-Don Han
Andrew Norman	Gabriel Veith	Kevin Gallagher	Seoung-Bum Son
Andriy Zakutayev	Ganesan Nagasubramanian	Kevin Wood	Shuo Zhang
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Baris Key	Harvey Guthrey	Kyle Fenton	Tingzheng Hou
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Chun Sheng Jiang	James Ciszewski	Nathan Neale	Yangping Sheng
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Claus Daniel	Javier Bareno	Pauls Stradins	Zhengcheng Zhang
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David Wood	Jing Xu	Phil Ross	



Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Brian Cunningham and David Howell

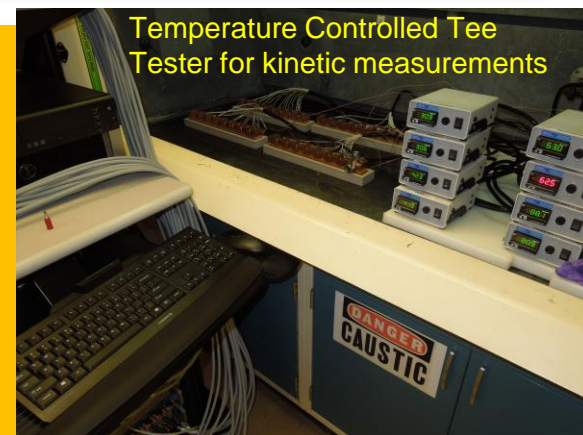


Remaining Challenges/Barriers

- Resolve issue of existence of silicates
- Establish baseline of kinetic parameters
- Move from chemical to electrochemical (lithation)
- Improved impedance models for growth of film
 - Once a film starts to form, it's not truly a flat surface anymore; diffusion becomes more complex, need to introduce this to models
- Better, direct measurements of formation of compliant layer

Future Research

- Set up and conduct temperature based soaking experiments with impedance to back out rate limiting steps
- Coordinate with spectroscopic/analytical tools to allow for real time observation of film and electrolyte



Q3FY18

- Further investigate the sudden change in impedance; correlate this to the appearance of the change in compliance

Q4FY18

- Move to real time spectroscopic and chemical analysis of films to capture rise of compliant layer
- Work with powder research efforts to verify if this happens on real powders



- Standard samples are being made and used for silicates (single source)
- Initial studies do indicate that the presence of silicates produces markedly different evolution compared to SiO_2
- Some evidence (EC-AFM, SIMS, EIS) for a change in the layers of the film that affect subsequent behavior
- Moving towards kinetics of growth of SEI, plus impact of lithation